"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

Action of chloro- and bromomalonic ester on salts of diethylphosphorous acid. A. E. Arbuzov and V. S. Abramov. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1946, 223-4.—To $(EtO)_2PONa$ (from 0.4 g. Na and 2.4 g. $(EtO)_2POH$ in 50 ml. Et_2O) was added slowly 4 g. $(EtO_2C)_2CHBr$ in Et_2O; a vigorous action ensued and rapid pptn. of NaBr took place; after the addn. the mixt. was heated 15 min. on a water bath, the cooled mixt. treated with H_2O, and the org. layer evapd., giving 4 g. crude (1.95 g. pure) $[CH(CO_2Et)_2]_2$ (I) (73% yield). Use of $(EtO)_2POK$ in a similar expt. gave 86% I. When $(EtO_2C)_2CHCl$ was used, however, $(EtO)_2PONa$ reacted slowly and required 2 hrs. boiling until 2.75 g. NaCl pptd.; in 1 expt. the org. filtrate gave 7% I, in other expts. I could not be isolated at all. The same result was obtained with $(EtO)_2POK$. No other identifiable substances were isolated. In an attempt to det. whether the formation of free radicals of (EtO_2C) and Ph_2C (previously observed in similar reactions of Ph_2CBr (*J. Russ. Phys.-Chem. Soc.* 61, 1923(1929)) precedes the formation of the dimeric products or the former arise from diasocn. of the latter, the following expt. was performed. To $(EtO)_2PONa$ (from 0.6 g. Na and 3.7 g. $(EtO)_2POH$) in Et_2O was added a mixt. of 3 g. $(EtO_2C)_2CHBr$ and 4.2 g. Ph_2CBr; immediately the golden color of Ph_2C became visible; after brief standing in contact with air, an abundant pptn. of $(Ph_2C)_2O_2$, m. 180° (from EtOH), took place. Distn. of the filtrate gave a small amt. of I, m. 74.5-5.5° (from dil. EtOH). Since no $Ph_2CCH(CO_2Et)_2$ was found, it was concluded that the course of the reaction is more complex than mere sepn. of NaX and formation of free radicals. G. M. K.

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ABRAMOV, V.S.

Reaction of halogen compounds with cyclones. Abramov, V. S. and K. A. Shoushinskaya. Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1946, 455-7. Cyclone (tetraphenylcyclopentadienone) (0.5 g.) and 15 ml. $(CH_2Cl)_2$ heated in a sealed tube 45 hrs. at 155° and 12 hrs. at 200-20° gave 80% *1,2,3,4-tetraphenylbenzene*, m. 180-90° (from MeOH-C_6H_6); a 30% yield is obtained in a similar reaction using $(CH_2Br)_2$. Heating 1 g. cyclone and 20 ml. *sym*-$Cl_2C_2H_2$ 35 hrs. at 250-70° gave 20% *1,2,-3,4-tetraphenyl-5,6-dichlorobenzene* (I), m. 241-2° (from MeOH-C_6H_6). Cyclone was unchanged on heating in a sealed tube with 10% HCl up to 250° and with C_6H_6-HCl to 300°. Cyclone (1.3 g.), 3 ml. CCl_4-CHCl and 15 ml. C_6H_6 heated 13 hrs. at 180-200° gave 92% I. Heating 1 g. acrycyclone with 20 ml. $(CH_2Br)_2$ 54 hrs. at 200-40° gave 0.51 g. unreacted cyclone and 0.04 g. *1,4-diphenyl-2,3-naphthylenebenzene*, m. 156-8° (from EtOH). The reactions described above apparently go through 2 steps: the halide breaks down to the corresponding unsatd. halide, which then adds to the cyclone as in an ordinary diene synthesis. G. M. Kosolapoff

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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ABRAMOV, V. S.

PA47T7

USSR/Chemistry - Synthesis, Diene 1 Mar 1948
Chemistry - Cyclic Compounds

"Diene Synthesis of Cyclic Compounds by the Dialkylacetylides of Mercury," V. S. Abramov, L. A. Shapshinskaya, 2 pp

"Dok Akad Nauk SSSR, Nova Ser" Vol LIX, No 7

As dienophyl, authors chose dialkylacetylenides of mercury: First, to test whether or not they react with dienes, and secondly, in case the reaction takes place, to synthesize polycyclical dimercurial organic compounds with their help, where the atoms of mercury stand in O-position and the synthesis is difficult by other methods. Report results breifly. Submitted by Academician A. Ye. Arbuzov, 23 Dec 1947.

[redacted]

47T7

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

62,

Diene synthesis with cyclones. A. S. Abramov. *Doklady Akad. Nauk SSSR* [illegible] 637 (1948). cf. A. and Tsyplenkova, *C.A.* **39**, 1689. On the basis of the previously reported diene syntheses with several substituted cyclones and ethylene dienophilic agents of type $CH_2:CHX$ it is suggested that the reactions involve the primary addn. of the CH_2— end of the reagent to 1 of the conjugated C atoms of the cyclone to give a tautomeric system in the incipient bridge, between C:CO:C and ⁻C:CO:C forms, to the latter of which is then drawn the electrophilic α C atom of the adduct to complete the synthesis. In all cases the final products were hydrocarbons, resulting from the loss of the endocarbonyl bridge and HX. The loss of the endocarbonyl bridge appears to be a simple elimination of CO by electron transfer from the terminal C atom of the original conjugated-bond system of the cyclone to the O of the CO group. The loss of HX may be simultaneous with the loss of CO or at another period; the data on hand do not permit a definite conclusion. Phencyclone in being able to yield complete adducts must be regarded in a different light from the other cyclones; its adducts are stable up to their m.ps., when CO is lost. This stability may be explained by the tendency to form the stable phenanthrene-type ring system. Thermal decomp. of its adducts in high-boiling solvents gave a hydrocarbon deriv. of tricyclone, and attempts to produce the loss of only CO, to be followed by dehydrogenation, failed.

G. M. Kosolapoff

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

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Alkoxy-substituted esters of phosphorous acid and their reaction with halosubstituted ethers. V. S. Abramov and N. F. Tvapitsyna. *Zhur. Obshchei Khim.* (J. Gen. Chem.) **19**, 929-38 (1949). -Addn. of 1 mol. PCl_3 to 114 g. (3 mols.) $MeOCH_2CH_2OH$ in 182 g. (3 mols.) pure Me_2NPh and 350 ml. Et_2O with cooling, followed by stirring 0.5 hr. and filtration, gave 71% $(MeOCH_2CH_2O)_3P$ (I), b_4 138.5-40.0°, n_D^{20} 1.4402, d_4^{20} 1.096; this (2 g.) was treated with 1.5 g. CuI (temp. rise to 45°) and the mixt. warmed until a clear soln. formed, but cooling failed to give a cryst. adduct; heating 7.4 g. ester with 4 g. $MeOCH_2CH_2Br$ 10 hrs. at 140-50° gave 60.8% (4.5 g.) $MeOCH_2CH_2PO(OCH_2CH_2OMe)_2$, b_1 155-6.5°, n_D^{20} 1.4302, d_4^{20} 1.1435; this (2.5 g.) heated with 10 ml. 10% HCl several hrs. at 130-50° gave an upper layer of Methyl Cellosolve and an aq. layer presumably contg. $MeOCH_2CH_2PO(OH)_2$, although evapn. failed to yield a cryst. product; addn. of 3.4 g. $MeOCH_2Br$ to 7 g. I gave a vigorous reaction and the mixt. heated 1.5 hrs. to 150° gave 3.5 g. $MeOCH_2PO(OCH_2CH_2OMe)_2$, b_7 154-6°, b_{14} 163-4°, n_D^{20} 1.4375, d_4^{20} 1.1456, which on hydrolysis with 10% HCl at 120-50° failed to give a cryst. acid. Similarly, 7 g. I and 3.8 g. $EtOCH_2Br$ in 1.5 hrs. at 150° gave 4.2 g. $EtOCH_2PO(OCH_2CH_2OMe)_2$, b_{11} 163-9.5°, n_D^{20} 1.4373, d_4^{20} 1.1258, which also failed to give a solid acid after 10 hrs. with 10% HCl at 130-50°. $PrOCH_2Br$ (5 g.) and 8 g. I gave in 1.5 hrs. at 150-72° $PrOCH_2PO(OCH_2CH_2OMe)_2$, b_{11} 157-9°, n_D^{20} 1.4389, d_4^{20} 1.101. Similar reaction in the cold of 51 g. PCl_3, 100 g. $EtOCH_2CH_2OH$, and 135 g. Me_2NPh in 320 ml. Et_2O gave after 3.5 hrs. 75% $(EtOCH_2CH_2O)_3P$, b_9 156-8°, n_D^{20} 1.4377, d_4^{20} 1.031, which also failed to form a solid cuprous iodide adduct. The ester (II) (8.2 g.) and 3 g. $EtOCH_2CH_2Br$ after 5 hrs. at 150-60° gave 7.5 g. $EtOCH_2CH_2PO(OCH_2CH_2OEt)_2$, b_9 181-4°, n_D^{20} 1.4372, d_4^{20} 1.089, which failed to give a solid acid on hydrolysis with 10% HCl (10 hrs. at 140-60°). II (8 g.) and 3.4 g. $MeOCH_2Br$ gave after 2 hrs. at 150° 6.5 g. $MeOCH_2PO(OCH_2CH_2OEt)_2$, $b_{0.4}$ 155-6°, n_D^{20} 1.4315, d_4^{20} 1.0877 (failed to give a solid acid on heating with 10% HCl to 140-60°); similarly $EtOCH_2Br$ gave 6.5 g. $EtOCH_2PO(OCH_2CH_2OEt)_2$, b_{11} 169-70°, n_D^{20} 1.4340, d_4^{20} 1.072 (also failed to give a solid acid), while 10 g. II and 5.1 g. $PrOCH_2Br$ gave in 1.5 hrs. at 150-60°, 7.7 g. $PrOCH_2PO(OCH_2CH_2OEt)_2$, b_9 158.5-59°, n_D^{20} 1.4364, d_4^{20} 1.055, which also failed to give a solid acid.

G. M. Kosolapoff

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Abramov, V. S.

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17

Alkoxyisopropyl esters of phosphorous acid and their properties. V. S. Abramov and E. N. Nikolaeva (Kazan State Univ.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) **20**, 100-6(1950).—*MeCH(OH)CH₂OEt*, b. 130-1°, n_D^{20} 1.4054, d_4^{20} 0.894 (from EtOH and propylene oxide in the presence of NaOH (90 g.), 105 g. Me_3NPh, and 300 ml. Et_2O treated with ice cooling dropwise with 30 g. PCl_3 gave 70%; $[Me(EtOCH_2CHO)_3P]$ (I), b. 150-8°, n_D^{20} 1.4320, d_4^{20} 0.983; I with *CaI* reacted spontaneously, yielding a sirupy *adduct*, sol. in Et_2O. [In the following, R = $CH(CH_2OEtOMe)$.] I (5.3 g.) heated with 0.05 g. *EtOCH₂CHMeBr* [b. 32-4°, n_D^{20} 1.4410, d_4^{20} 1.240, from $MeCH(OH)CH_2OEt$ and PBr_3] to 120° 0.5 hrs. in a sealed tube gave *EtOCH₂CHMeP(O)(OR)₂*, b. 102-4° (vacuum unstated), n_D^{20} 1.4320, d_4^{20} 1.012. Similarly, 10 g. I treated slowly with 3.7 g. $BrCH_2OMe$, then kept 1-2 hrs. at 120°, gave 4.8 g. *MeOCH₂PO(OR)₂*, b. 105-8°, n_D^{20} 1.4272, d_4^{20} 1.049. Similarly, 10 g. I and 4 g. $BrCH_2OEt$ gave 3.9 g. *EtOCH₂PO(OR)₂*, b. 161-6°, n_D^{20} 1.4312, d_4^{20} 1.040, while $BrCH_2OPr$ likewise yielded *PrOCH₂PO(OR)₂*, b. 158-60°, n_D^{20} 1.4310, d_4^{20} 1.029, and $BuOCH_2Cl$ gave *BuOCH₂PO(OR)₂*, b. 210-13°, n_D^{20} 1.4309, d_4^{20} 1.013. *Iso-PrOCH₂CHOHCHMe*, b. 137-8°, n_D^{20} 1.4070, d_4^{20} 0.879 (from propylene oxide, NaOH, and iso-PrOH as above; 150 g.) with 19.4 g. PCl_3 in the presence of 51.2 g. Me_3NPh in 150 ml. Et_2O gave 18 g. crude product (b. 140-8°), the combined yield of 2 expts. treated with Na to remove diethyl phosphite, yielded pure [*Me(iso-PrOCH₂CHO)₂P*], b. 152-5°, n_D^{20} 1.4400, d_4^{20} 0.9515. $PhOCH_2CH_2OH$, b. 118-21° (250 g.), and 164 g. Me_3NPh in 500 ml. Et_2O treated with 62.2 g. PCl_3 in the cold and filtered from the amine HCl, gave a product which decomposed on attempted distn., yielding a yellow mass contg. P and some PhOH. Addn. of 45.2 g. PCl_3 in the cold to 80 g. $EtOCH_2CHOHOMe$ and blowing with dry air gave 25 g. *(EtOCH₂CHMeO)₂POH*, b. 135-7°, n_D^{20} 1.4270, d_4^{20} 1.049; similar use of 100 g. $PhOCH_2CH_2OH$ and 33.2 g. PCl_3 gave *(PhOCH₂CH₂O)₂POH*, as an undistillable residue, after the removal of $POCl_3$, $PhOCH_2CH_2Cl$ and $CHCl_3$. However, addn. of 45 g. $PhOCH_2CH_2OH$ to 41.8 g. PCl_3, followed by blowing with air, gave 21 g. *PhOCH₂CH₂OPCl₂*, b. 150-2°, n_D^{20} 1.5437, d_4^{20} 1.428.

G. M. Kosolapoff

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CA

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Reaction of dialkyl phosphites with aldehydes and ketones (a new method of synthesis of esters of hydroxyalkanephosphonic acids). V. S. Abramov (S. M. Kirov Chem.-Technol. Inst., Kazan). *Doklady Akad. Nauk S.S.S.R.* **73**, 487-9(1950). The prepn. of hydroxyalkanephosphonic acids is reviewed and the mechanism of formation of $RPO(OR)_2$ from RX and $(RO)_2PONa$ is discussed. The latter reaction is believed to proceed by addn. of RX to $(RO)_2PONa$ (based on trivalent P) to yield $(RO)_2P(ONa)(R)X$; this view is supported by the formation of such adducts with $(MeOCH_2CH_2O)_2PONa$ (undescribed) and in reactions of LiBr or LiI with $ROCH_2PO(OR)_2$ (also undescribed), at high temps. The reaction is believed to proceed by addn. of the cationoid C atom of the RX to the unshared electron pair of P, yielding a positively charged central P atom, to which the neg. X ion adds in completion of the reaction. The adduct then may cleave either RX or NaX, thus yielding $RO(NaO)P(O)R$ or $RPO(OR)_2$, the direction of the cleavage being detd. by the nature of the radical R directly bound to P, by the nature of the halide X, by the nature of the OR radicals, and by the exptl. conditions. Another mechanism that is possible is shown by the equation $(RO)_2PONa + R'X \rightarrow (RO)_2P(ONa)R \rightarrow (RO)_2P(O)R + Na^+ + X^-$. The latter interpretation leads to the possibility of reactions of $(RO)_2PONa$ with other compds. that polarize analogously to RX; among these are aldehydes and ketones, in which the C of the CO group becomes cationoid, permitting the formation of adducts of the type $(RO)_2P(O)CR_2O^-Na^+$, which with acidified H_2O yield $(RO)_2P(O)CR_2OH$. The reaction is catalyzed by a few drops of MeOLi or MeONa, which is added to the mixt. of the dialkyl phosphite and the carbonyl compd., thus permitting a rapid chain reaction in which unused $(RO)_2POH$ removes the Na from the intermediate adduct. The yields are improved when the radicals composing the carbonyl compd. increase polarization of the CO group (thus, BzH gives a theoretical yield). Some 30 new esters were prepd. (none are described), in which *Me*, *Et*, and *iso-Pr* radicals are present in the ester group of $(RO)_2P(O)C(OH)R'R''$, while R' is *H* and R'' is either *H*, *Me*, *Pr*, or *Ph*; also mentioned are compds. with $R' = R'' =$ *Me*, as well as *cyclopentyl* and *cyclohexyl* analogs. All esters were either cryst. solids or very viscous liquids. Dehydration of the products may yield unsatd. esters while replacements of OH by OR may yield the corresponding alkoxyalkanephosphonates. G. M. Kosolapoff

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ABRAMOV V.S.

10

Action of halogen substituted ethers on the sodium salts of [illegible]-alkoxyethyl phosphorous acids. V. S. Abramov and [illegible] Kazan State Univ. [illegible] Zhur. Obshchei Khim. 21, [illegible] (1951). Chem. Abs. 46, [illegible] d. CA 47, [illegible] 41, [illegible] — Addn of [illegible] PCl3 to [illegible] MeOCH[illegible] CH2OH with [illegible] 6 hr [illegible] removing [illegible] the HCl, and [illegible] gave [illegible] MeOCH[illegible] HCl, b. [illegible] 30, and [illegible] (MeOCH[illegible] HO)2POH, b. [illegible] at 1 [illegible] This [illegible] absorbed [illegible] react with [illegible] Na [illegible] in [illegible] EtO was heating [illegible] the Na deriv. which with MeOCH2CH2Cl [illegible] to give any NaCl [illegible] of MeOCH2CH2[illegible] [illegible] of NaBr [illegible] after [illegible] hr on a steam bath [illegible] of the [illegible] water, removal of the NaBr, yielded a residue of MeOCH2CH2O(Na)PO(OH)OMe, from EtOH-EtO. Similarly, EtOCH2Br gave [illegible] MeOCH2CH2O(Na)PO(OH)Et, while PrOCH2Br gave [illegible] (MeOCH2CH2O(Na)PO(OH)Pr, and BuOCH2CH2Cl gave 65% MeOCH2CH2O(Na)PO(OH)Bu. PCl3 (53.3 g.) with [illegible] g. EtOCH2CH2OH gave 66% (EtOCH2CH2O)2POH, b. [illegible] at 1.4[illegible] 1.4[illegible], which with Na, as above, followed by treatment with ROCH2Br and [illegible] gave 3[illegible] (EtOCH2CH2O)2PO(OH)Me, 72% EtOCH2CH2O(Na)PO(OH)Et, and 86% (EtOCH2CH2O)2PO(OH)Pr. Reaction of 7 g. MeOCH2CH2O(Na)PO(OH)Pr with [illegible] g. Na in EtO, followed by 3.5 g. EtCl, [illegible] gave a small amount of distillate [illegible] and a viscous residue which on [illegible] by [illegible] in dry EtOH gave 85% Lew pure MeOCH2CH2O(Na)PO(OH)CH2CH2Me. The reaction of the last homologs is believed to occur by addn of some NaX across the P=O link with subsequent displacement of the R radical of the ester by the new X atom. G. M. K.

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CA ABRAMOV, V.S.

Organic Chemistry 10

Action of halogen derivatives on bis(2-n-thoxyethyl) sodium phosphite. V. S. Abramov and E. A. Kulikova (Kazan State Univ.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 23, 257-7(1953), cf. *C.A.* 46, 6082a.—[R = MeOCH$_2$CH$_2$ throughout.] Addn. of 5 g. PhCH$_2$Cl to (RO)$_2$PONa (from 5 g. (RO)$_2$POH) in 30 ml. BuAc, brief heating, and distn. *in vacuo* gave a trace of product, b_{10} 180-8°, n_D^{20} 1.4708, apparently PhCH$_2$PO(OR)$_2$; the residue was NaCl. The reaction run on a larger scale with prolonged heating gave 55% of the above ester, b_{11} 190-3°, n_D^{20} 1.4970, d_4^{20} 1.165, if the NaCl was removed before the distn. A similar reaction with PhCH$_2$Br without removal of NaBr prior to distn. gave a trace of distillable matter; the residue was glassy ROP(O)(ONa)CH$_2$Ph (80.8% yield). Similarly EtBr without removal of the NaBr gave 56.5% EtP(O)(OR)$_2$, b_5 152-4°, n_D^{20} 1.4538, d_4^{20} 1.114; the distn. residue was NaBr. AcBr gave a little RBr, b_{10} 60-2°, n_D^{20} 1.4320, d_4^{20} 1.392, while the distn. residue was 93% glassy product, possibly MeC(OAc)[P(:O)(ONa)OR]$_2$. AcCl gave a little RCl, b_{11} 42-6°, and 75% glassy di-Na salt similar to the above. (RO)$_2$PONa, from 5 g. (RO)$_2$POH, with 4.5 g. (CH$_2$Br)$_2$ gave a ppt. of NaBr only after long refluxing and total distn. gave a little RBr and 76% glassy [CH$_2$P(O)(ONa)OR]$_2$ (from abs. EtOH). Addn. of 3.4 g. (CH$_2$Br)$_2$ to (EtO)$_2$PONa, from 5 g. (EtO)$_2$POH, gave a ppt. of NaBr only after heating and distn. gave unstated yields of [CH$_2$P(O)(OEt)$_2$]$_2$ (cf. Ford-Moore and Williams, *C.A.* 42, 2220g), solid distn. residue which appeared to be the di-Na salt of the di-Et ester of the above acid. If (EtO)$_2$PONa from 5 g. (EtO)$_2$POH is added to 16 g. (CH$_2$Br)$_2$ in Et$_2$O and the mixt. is refluxed, distn. of the entire mass gives a Br-contg. solid, apparently BrCH$_2$CH$_2$P(O)(ONa)OEt. Apparently the reaction of the pptd. NaX on heating with the phosphonic acid esters, to form the partial Na salts of the latter, requires a polar group in the radical of the phosphonate. G. M. Kondagoff

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ABRAMOV, V. S.

"Interaction of dialkylphosphorous acids with aldehydes and ketones. New method for the preparation of esters of hydro-xyalkyl-phosphinic acids." (p. 647)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1952, Vol. 22, No. 4, pp 709-713

(Inst. Chem. Technol., Kazan)

co: authors: S.M. KIROV

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ABRAMOV, V. S.

Abramov, V. S.; Samoilova, O. D.- "Action of lithium halides on esters of phosphorous acid." - (p. 912), 913

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1952, Vol. 22, No. 6

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ABRAMOV, V.S.

Chemical Abst.
Vol. 48 No. 5
Mar. 10, 1954
Organic Chemistry

The action of halide salts of alkali metals on the esters of alkanephosphonic acids. V. S. Abramov and O. D. Samoilova (State Univ., Kazan). *J. Gen. Chem. U.S.S.R.* 22, 971-3(1952)(Engl. translation). See *C.A.* 47, 4838*d*.
H. L. H.

AF 7-28-54

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

ABRAMOV, V.S.; SHAPSHINSKAYA, L.A.

Diene synthesis with anisylcyclone and some other cyclones. Zhur. Obshchey Khim. 22, 1450-7 '52. (MLRA 5:8)
(CA 47 no.20:10488 '53)

1. Kazan State Univ.

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231T4

USSR/Chemistry - Organophosphorus Compounds May 52

"Some Properties of Alpha-Hydroxyalkylphosphonic Acid Esters," V. S. Abramov, L. P. Semenova, L. G. Semenova, Kazan Chem Tech Inst imeni S. M. Kirov

"Dok Ak Nauk SSSR" Vol 84, No 2, pp 281-284

Authors find the C - P bond in alkylphosphonic acid esters is very stable. Note that esters of alpha-hydroxyalkylphosphonic acids, however, readily undergo fission of the C - P bond in alk solns to form ketones or aldehydes. The methyl and ethyl esters of alpha-hydroxybenzylphosphonic acids formed dimethyl and diethyl phosphorous acids, resp. Distn of alpha-hydroxyalkylphosphonic acid esters is accompanied by a partial decompn. A thermal equil exists between alpha-hydroxyalkylphosphonic acid esters and the materials from which they were synthesized. (aldehydes or ketones and dialkylphosphorous acids). States that, under distn, this equil is apparently shifted to the side of the starting materials. Heating of the ethyl ester of alpha-hydroxy-alpha-methylbenzylphosphonic acid results in its decompn to diethylphosphorous acid and acetophenone. Presented by Acad A. Ye. Arbuzov 10 Mar 52

ABRAMOV, V. S.

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231T4

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

ABRAMOV, V. S.

Reaction of dialkyl phosphorous acids with aldehydes and ketones. II. Methyl and propyl esters of α-hydroxyalkylphosphonic acids. V. S. Abramov and L. P. Semenova (S. M. Kirov Chem. Technol. Inst., Kazan). *Sbornik Statei Obshchei Khim., Akad. Nauk S.S.S.R.* 1, 303-7 (1953); cf. *C.A.* 45, 2355h; 48, 8169d.—Equimolar mixts. of $(RO)_2POH$ and the aldehyde or ketone were treated with a few drops of satd. MeONa; the temp. rise was usually 30-100°, and the product could be distd. immediately thereafter; heating of the mixt. is unnecessary. Thus were obtained the following ($(MeO)_2P(O)CR_1R_2R_3$ (R_1, R_2, R_3, % yield, b.p., d_{20}, n^{20}_D given): H, OH, Me, 62.5, 138°/18, 1.2314, 1.4400; H, OH, Pr, 59.8, 143-5°/59.8, 1.1438, 1.4379; H, OH, CH_2CHMe_2, 53.4, 159-60°/14, 1.0707, 1.4390; Me, Me, OH, 65.8, —, —, — (m. 72-3°); OH, Et, Me, 60, 141-2°/13, 1.1380, 1.4380; OH, CH_2Ph; CH_2Ph, 50.6, —, —, — (m. 125°); OH, Ph, Ph, 56, —, —, — (m. 103-4°); for $(PrO)_2P(O)CR_1R_2R_3$: H, OH, Me, 42, 155-60°/10, 1.200, 1.4306; H, OH, Pr, 37.4, 171-2°/15, 1.0281, 1.4364; H, OH, Ph, 31.6, 127-8°/9, 1.070, 1.4671; OH, Me, Me, 59.5, 138°/0, 1.048, 1.4335; OH, Et, Me, 61, 148°/9, 1.0366, 1.4390; OH, Me, Ph, 78.8, 171°/9, 1.067, 1.4765; OH, $(CH_2)_4$, 58.6, 168°/9, 1.071, 1.4491; OH, $(CH_2)_5$, 44.3, 179°/9, 1.030, 1.4307. Reaction of 11 g. $(MeO)_2POH$ with 12.2 g. salicylaldehyde in which the addn. of some MeONa gave a temp. rise of 23° gave after heating on a steam bath a wavy mass, which could not be recrystd. or distd. Although the reactions of $(MeO)_2POH$ with Et_2CO, MePrCO and 3,3-dimethyl-2-butanone gave moderate rise in temp., the products could not be isolated owing to evolution of the starting materials during distn. A very vigorous reaction took place between $(PrO)_2POH$ and [illegible] of MeONa, but the yellow solid product could [illegible] or distd. without decompn. It is suggested that [illegible] increased complexity of the ketone the reaction is [illegible] hindered. III. Isopropyl and isobutyl esters of [illegible] alkylphosphonic acids. V. S. Abramov [illegible] *Ibid.* 398-403.—The reaction [illegible] previous abstr. gave the following (iso-$PrO)_2P(O)CR_1R_2R_3$: [illegible] H, OH, Me, 88, 153-5°/17, 1.0167, 1.4252; [illegible] 65.3, 140-7°/10, 1.0166, 1.4312; H, OH, CH_2CHMe_2; [illegible] 154-6°/12, 0.9965, 1.4317; H, OH, C_6H_4OMe-[illegible] 180-2°/8, 1.1490, 1.4870; OH, Me, Me, [illegible] (m. 53-4°); OH, Et, Me, 48.4, 138-40°/13, 1.0271, [illegible] H, OH, Me, 46, 160-2°/12, 1.0092, 1.4312; (iso-$BuO)_2P(O)CR_1R_2R_3$: H, OH, Pr, 60.3, 165-7°/8, 0.9891, 1.[illegible] H, OH, CH_2CHMe_2, 74.7, 172-3°/7, 0.9888, 1.4379; [illegible] Me, Me, 39.4, 153-4°/13, 1.0036, 1.4317; OH, Me, [illegible] 152-4°/9, 1.0080, 1.4377; OH, $(CH_2)_5$, 81.3, [illegible] 1.0498, 1.4540; OH, $(CH_2Ph)_2$, 16.4, —, —, — (m. 11[illegible] 11°). The reaction product of (iso-$PrO)_2POH$ and salicyl aldehyde could not be satisfactorily purified; the reaction with Et_2CO gave a good temp. rise but the product decomposed on attempted distn. yielding the starting materials; similarly unsuccessful was the reaction with AcPh, with either MeONa, LiOMe or KOMe catalysts. Reaction of (iso-$BuO)_2POH$ with Et_2H gave a good temp. rise and yielded crude product in low yield, b_9 145-9°, with decompn.; attempted redistn. failed to give a better product. The reaction with AcPh again led to decompn. of the product. Generally the more complex aldehydes and ketones are unsatisfactory. The temp. rise of 30-40° in these reactions was shown to occur during the actual coupling step, since the reaction of $(RO)_2PONa$ with MeONa gives a temp. rise of but 1-2°. G. M. Kosolapoff

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ABRAMOV, V. S. AND KUGNETSOV, N. S.

Interaction of Dialkyl Phosphorous Acids with Aldehydes and Ketones. III. Isopropyl and Isobutyl Esters of β-Hydroxyalkyl Phosphinic Acids, page 398
Sbornik statey po obshchey khimii (Collection of Papers on General Chemistry), Vol I, Moscow-Leningrad 1953, pages 762-766

Kazan Chemico-Technological Inst imeni S. M. Kirov

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ABRAMOV, V.S.

P (4)

Chemical Abst.
Vol. 48 No.5
Mar. 10, 1954
Organic Chemistry

Reaction of dialkyl phosphorous acids with aldehydes and ketones. IV. Butyl and allyl esters of α-hydroxyalkylphosphonic acids. V. S. Abramov, R. V. Dmitrieva, and A. S. Kaoustina (S. M. Kirov Chem. Technol. Inst., Kazan). *Zhur. Obshchei Khim.* 23, 257-62(1953); cf. *C.A.* 47, 5361c. —$(RO)_2POH$ with aldehydes and ketones in the presence of RONa yield addn. products of the general type $(RO)_2P(O)C(OH)R'R''$, as evidenced by heat evolution on mixing the ingredients. However, distn. of the reaction mixt. generally leads to decompn. and isolation of the starting materials; this is especially true for phosphites with large R units. (The text of the article is not clear, for statements concerning very ready isolation of the hydroxyphosphonates and the impossibility of their isolation are made side by side—G.M.K.) The reactions were run by adding a few drops of MeOH-MeONa to equimolar mixts. of di-Bu or diallyl phosphites and the desired carbonyl compd. and distg. the mixts. after brief standing and/or heating. The following were obtained [yield (%), b.p./mm., d_{20}, and n_D^{20} given]: $(BuO)_2P(O)CH(OH)Me$, 56.7, 162-3°/9, 1.024, 1.4384; $(BuO)_2P(O)CH(OH)Pr$, 49, 168-70°/6, 1.000, 1.4400; $(BuO)_2P(O)CH(OH)CH_2CHMe_2$, —, 180-2°/11, 0.998, 1.4360; $(BuO)_2P(O)CH(OH)Ph$, —, 168-70°/5, 1.026, 1.4680; $(BuO)_2P(O)CMe_2OH$, 59.2, 154-5°/7, 1.018, 1.4360; $(BuO)_2P(O)CEtMeOH$, 57.7, 156-7°/8, 1.015, 1.4403; $(BuO)_2P(O)CMePhOH$, 30, 179-80°/9, 1.025, 1.4670; $(BuO)_2P(O)CPh_2OH$, —, 207-9°/7, 1.031, 1.4760; $(BuO)_2P(O)C(OH)(CH_2)_4$, 40.4, 179-80°/9, 1.049, 1.4549; $(BuO)_2P(O)C(OH)(CH_2)_5$, 48.7, 178-80°/7, 1.039, 1.4570; $(CH_2{:}CHCH_2O)_2P(O)CHMeOH$, 65.3, 151°/10, 1.1187, 1.4565; $(CH_2{:}CHCH_2O)_2P(O)CH(OH)Pr$, 31.6, 163-4°/10, 1.0769, 1.4552; $(CH_2{:}CHCH_2O)_2P(O)CMe_2OH$, 38.8, 132°/12, 1.0907, 1.4500; $(CH_2{:}CHCH_2O)_2P(O)C(OH)(CH_2)_4$, 45.7, 165-7°/7, 1.1253, 1.4740; $(CH_2{:}CHCH_2O)_2P(O)C(OH)(CH_2)_5$, 67.7, m. 56.5-7.0°. Addn. of few drops MeONa-MeOH to 9.7 g. $(BuO)_2POH$ and either 4.3 g. MePrCO, 4.3 g. Et_2CO, or 9.1 g. $(PhCH_2)_2CO$ gave a temp. rise to 47-48°;

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after being heated to 120-30°, the reaction mixts. on attempted distn. gave only the starting materials. Reaction with iso-BuCHO gave similar results. Diallyl phosphite and iso-BuCHO also gave only the starting materials, although the original mixt. appeared to react normally; BzH also failed to yield the desired ester with diallyl phosphite since during attempted distn. the mass decompd. at 170°, yielding a foamy solid; only starting products were obtained from diallyl phosphite and either EtEtCO or AcPh. $(BuO)_2POH$ with Et 2-oxocyclopentane carboxylate (in the presence of MeONa) gave, after unstated period at 140-50°, only small amts. of the starting materials and much tar.

G. M. Kosolapoff

MF 7-14-51

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ABRAMOV, V. S.

ABRAMOV, V. S.

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Reaction of dialkyl phosphorous acids with aldehydes and ketones. V. 2-Methoxyethyl and 2-ethoxyethyl esters of (1-hydroxyalkyl)phosphonic acids. V. S. Abramov, Yu. A. Bochkova, and A. D. Pokrakova (S. M. Kirov Chem.-Tech. Inst., Kazan). Zhur. Obshchei Khim. 25, 1010-3 (1955); cf. C.A. 47, 9227f, 5351e; 48, 2572. — (ROCH_2-CH_2O)$_n$POH react with aldehydes and ketones with much evolution of heat in the presence of catalytic amts. of MeO-Na soln.; however the expected esters of (hydroxyalkyl)-phosphonic acids undergo decomp. or dissoc. to the initial reactants on attempted vacuum distn. (only the product from Me_2CO could be distd.); hence the products were purified by contact with adsorbents such as Al_2O_3 or activated C in MeOH or C_6H_6. The ease of cleavage of the (1-hydroxyalkyl)phosphonates is ascribed to an intramol. H bond between the HO group and the phosphoryl group. Usually a lower temp. during the purification facilitates the isolation. The course of the reaction was followed by comparison of the phys. consts. of the initial reaction mixt. (without MeONa) with that of the final mixt.; the purification with AlO_3 was run by heating 1-2 hrs. on a steam bath, then with activated C also 1-2 hrs. on a steam bath, and distg. the solvent *in vacuo*. The products obtained (% yield, n_D^{20}, and d_{20} given): ($MeOCH_2CH_2O$)$_2$P(O)CH(OH)-Me, 79.9, 1.4401, 1.1681; ($MeOCH_2CH_2O$)$_2$P(O)CH(OH)Pr, 60.6, 1.4405, 1.1365; ($MeOCH_2CH_2O$)$_2$P(O)CH(OH)Ph, 69.7, 1.5055, 1.2241; *o*-$HOC_6H_4CH(OH)P(O)(OCH_2CH_2OMe)_2$, — (b$_{0.4}$ 125-59, 1.4975, —; ($MeOCH_2CH_2O$)$_2$P(O)CMe$_2$OH, — (b$_{0.4}$ 125-6°), 1.4345, 1.1573 (undistd. product, 66.4%, n_D^{20} 1.4365, d_{20} 1.1540); ($MeOCH_2CH_2O$)$_2$P(O)C(OH)(CH$_2$)$_4$, —, 1.4640, 1.1910; ($MeOCH_2CH_2O$)$_2$P(O)C(OH)(CH$_2$)$_5$, 55.8, 1.4660, 1.1648; ($EtOCH_2CH_2O$)$_2$P(O)CH(OH)Me, 67.3, 1.4430, 1.123; ($EtOCH_2CH_2O$)$_2$P(O)CH(OH)Pr, 53.1, 1.4476, 1.100; ($EtOCH_2CH_2O$)$_2$P(O)CH(OH)Ph, 69.5, 1.4988, 1.188; ($EtOCH_2CH_2O$)$_2$P(O)CH$_2$CH$_2$OEt, 59.7, —, —; *o*-$HOC_6H_4CH(OH)P(O)(OCH_2CH_2OEt)_2$, 54 (b$_{0.4}$ 144-5°), 1.4410, 1.097; ($EtOCH_2CH_2O$)$_2$P(O)CMe$_2$OH, 53, 1.4570, 1.135; ($EtOCH_2CH_2O$)$_2$P(O)C(OH)(CH$_2$)$_4$, 74.6, 1.4562, 1.110. MeEtCO, MePrCO, AcPh, Ph_2CO, ($PhCH_2$)$_2$CO and Bz$_2$ showed evidence of reaction but the desired products could not be isolated. G. M. Kosolapoff

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ABRAMOV, V. S.

6

(4)

Mechanism of the Arbuzov rearrangement. V. S. Abramov and G. Karp (S. M. Kirov Chem.-Technol. Inst., Kazan). *Doklady Akad. Nauk S.S.S.R.* 91, 1095-3 (1953).—The existence of the previously hypothetical addn. product of $(RO)_3P$ and RX in the Arbuzov reaction has been proven by isolation of such adducts between several $(RO)_3P$ and $EtOCHBrCH_2Br$. The adducts could not be crystd. and were obtained as viscous masses which on heating gave the expected RBr and the corresponding phosphonates; treatment of these adducts with H_2O also gave the same phosphonates. Thus were obtained the following esters, $(RO)_2P(O)CH(OEt)CH_2Br$ (R, % yield, b.p./mm., n_D^{20}, d_{20} given): *Me*, 64.4, 137-8°/13, 1.4648, 1.4402; *Et*, 74.1, 140-40.5°/0-0.5, 1.4570, 1.3180; *Bu*, 52.3, 176-8°/12-13, 1.4548, 1.1909; *iso-Bu*, 53.2, 170-1°/14-14.6, 1.4523, 1.1839; and *Ph*, —, m. 40-2°. The temp. necessary for decompn. of the intermediate $(RO)_2PR'Br$ rises with increase of the mol. wt. of the ester used. The results suggest that the Arbuzov reaction proceeds through the addn. step which goes by the bimol. mechanism, after which the adduct decomp. either by an intramol. mechanism or by ionization and a bimol. loss of RX. Cf. Pudovik, *C.A.* 47, 3226g. G. M. Kosolapoff

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ABRAMOV, V.S.

USSR/Chemistry - Reaction processes

Card 1/1 Pub. 151 - 22/36

Authors : Abramov, V. S., and Il'ina, N. A.

Title : Reaction of dialkylphosphorous acids with aldehydes and ketones. Part 6.- Esters of alpha-oxy-propylphosphinic acid.

Periodical : Zhur. ob. khim. 24/1, 124-127, Jan 1954

Abstract : The derivation of seven hitherto unknown esters of alpha-oxy-propylphosphinic acid from the reaction of dialkylphosphorous acids with propionic aldehyde is described. The structural characteristics and constants of these esters are tabulated. A freshly prepared saturated sodium-methylate solution served as catalyst for the above mentioned reaction. The effect of the hydrocarbon radical of the acid on the rate and process of reaction between dialkylphosphorous acid and carbonyl compounds is explained. Five USSR references (1905 -1953). Tables.

Institution : The S. M. Kirov Chemical-Technological Institute, Kazan

Submitted : May 10, 1953

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ABRAMOV, V. S.

USSR/Chemistry - Reaction processes

Card 1/1 Pub. 151 - 24/38

Authors : Abramov, V. S., and Kapustina, A. S.

Title : Reaction of dialkylphosphorous acids with aldehydes and ketones. Part 7.- Esters of alpha-hydroxy-(6-quinolyl)-methylphosphinic acid

Periodical : Zhur. ob. khim. 24/2, 311-314, Feb 1954

Abstract : The reaction of dialkylphosphorous acids with 6-quinoline-aldehyde was investigated. The derivation of seven new esters of alpha-hydroxy-(6-quinolyl)-methylphosphinic acid, separated from the reaction products in form of picrates is described. The properties of these esters are tabulated. The derivation of isopropyl ester of alpha-hydroxy-(6-quinolyl)-methylphosphinic acid, in form of colorless crystals with 119-120° melting point, is reported. Two USSR references (1950 and 1953). Tables.

Institution : The S. M. Kirov Chemical-Technological Institute, Kazan

Submitted : June 27, 1953

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ABRAMOV, V. S.

USSR/ Chemistry Reaction processes

Card : 1/1 Pub. 151 - 20/35

Authors : Abramov, V. S., and Pakhomova, A. P.

Title : Reaction of substituted vinyl ethers with cyclones

Periodical : Zhur. ob. khim. 24, Ed. 7, 1198 - 1203, July 1954

Abstract : The process of reaction between cyclones, acecyclones, phencyclones and alpha-substituted vinyl ethers (simple or complex), is described. On the basis of experimental results, it was established that the reaction between cyclones and alpha-substituted simple or complex vinyl ethers is similar to the reaction of diene synthesis but entirely different from the reaction of cyclones with beta-substituted ethers. The products obtained from such reactions, are listed together with their chemical properties. Nine references: 4 USSR, 4 German and 1 USA.

Institution : Chemical Technological Institute, Kazan

Submitted : February 6, 1954

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

ABRAMOV, V.S.

USSR/ Chemistry - Reaction processes

Card 1/1 Pub. 151 - 22/37

Authors : Abramov, V. S., and Karp, G. A.

Title : The mechanism of the Arbuzov regrouping. Reaction of alpha,beta-dibromodiethyl ether with phosphites

Periodical : Zhur. ob. khim. 24/10, 1823-1835, Oct 1954

Abstract : The reaction between alpha-beta-dibromodiethyl ether with phosphites was investigated. It was established that the Arbuzov regrouping, also for the case of aliphatic phosphites, takes place with the formation of an intermediate addition product, i. e., it takes place in two separate individual stages. The products formed during the heating of the addition products and their exposure to the effect of water are listed. The mechanism of the Arbuzov regrouping is described in detail. Seventeen references: 9-USSR; 6-USA and 2-German (1898-1953). Tables.

Institution: The S. M. Kirov Chemical-Technological Institute, Kazan

Submitted : May 18, 1954

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ABRAMOV, V.S.

USSR.

Reaction of aldehydes with phosphites [illegible]

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ABRAMOV, V.S.

6

V Reaction of dialkyl esters of phosphorous acids with aldehydes and ketones. VIII. Esters of hydroxy(3-cyclohexen-1-yl)methylphosphonic, hydroxy(4-methyl-3-cyclohexen-1-yl)methylphosphonic acid and hydroxy(3,4-dimethyl-3-cyclohexen-1-yl)methylphosphonic acid. V. S. Abramov and A. S. Nazmutdinova (Chem. Technol. Inst., Kazan). *Zhur. Obshchei Khim.* 25, 1141-6(1955); cf. *C.A.* 49, 4507a; 8278c.—Addn. of $(RO)_2POH$ to 1,2,5,6-tetrahydrobenzaldehyde and its homologs in the presence of MeONa, as described previously (*loc. cit.*), gave the following esters: *di-Me hydroxy(3-cyclohexen-1-yl)methylphosphonate*, n_D^{20} 1.4792, d_{20} 1.2200; *di-Et ester*, n_D^{20} 1.4715, d_{20} 1.1544; *di-iso-Pr ester*, m. 63-4°; *di-Bu ester*, n_D^{20} 1.4685, d_{20} 1.0810; *di-iso-Bu ester*, n_D^{20} 1.4668, d_{20} 1.0700; *di-Me hydroxy(4-methyl-3-cyclohexen-1-yl)methylphosphonate*, n_D^{20} 1.4875, d_{20} 1.1881; *di-Et ester*, n_D^{20} 1.4765, d_{20} 1.1331; *di-iso-Pr ester*, m. 79-83°; *di-Bu ester*, n_D^{20} 1.4675, d_{20} 1.0566; *di-iso-Bu ester*, n_D^{20} 1.4722, d_{20} 1.0638; *di-Et hydroxy(3,4-dimethyl-3-cyclohexen-1-yl)methylphosphonate*, n_D^{20} 1.4799, d_{20} 1.1270; *di-iso-Pr ester*, m. 60-2°; *di-Bu ester*, m. 48-50°. The larger is the R of the phosphite, the more complete is the reaction. Products were purified by washing with aq. $NaHSO_3$ and NaCl. None could be distd. Also in *J. Gen. Chem. U.S.S.R.* 25, 1095-98(1955)(Engl. translation).

G. M. K.

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ABRAMOV, V. S.

"Condensation of Dialkyl Phosphites with Substituted Aldehydes and Ketones"
Paper presented at the First Conference on Phosphorous Compounds, Kazan, 8-14 Dec 56

SO: E-3,084,841

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MISKAMOV, V.S.

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

ABRAMOV, V.S.; KHAYRULLIN, V.K.

Interaction of dialkylphosphorous acids with aldehydes and ketones. Part 9. Di-tret-(β', β', β'-trichloro)-butyl esters of substituted α-oxymethylphosphinic acid. Zhur.ob.khim. 26 no.3:811-813 Mr '56. (MLRA 9:8)

1. Kazanskiy khimiko-tekhnologicheskiy institut imeni S.M. Kirova. (Phosphinic acid)

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

ABRAMOV, V.S.; IL'INA, N.A.

Mechanism of the Arbuzov rearrangement. Part 3. Interaction of the nitrile and methyl ester of α,β-dibromo- and α,β-dichloropropionic acid with phosphites. Zhur.ob.khim. 26 no.7:2014-2019 Jl '56. (MIRA 9:10)

1. Kazanskiy khimiko-tekhnologicheskiy institut imeni S.M. Kirova. (Nitriles) (Rearrangements(Chemistry)) (Propionic acid) (Phosphites)

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ABRAMOV, V. S.

Esters of α-hydroxy-β-chloro-isopropylene phosphonic acid and 1,2-epoxy-2-propylphosphonic acid. V. S. Abramov

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

ABRAMOV, V. S. (Kazan Chem. Tech. Inst. im. S. M. Kirov)

"The Question of the Condensation of Dialkylphosphinous Acids with Substituted Aldehydes and Ketones" (K voprosu o kondensatsii dialkilfosforistykh kislot s zameshchennymi al'degidami i ketonami)

Chemistry and Uses of Organophosphorous Compounds
(Khimiya i primeneniye fosfororganicheskikh soyedneniy),
Trudy of First Conference, 8-10 December 1955, Kazan,
Published by Kazan Affil. AS USSR, 1957
pp. 218-222

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

ABRAMOV, V. S.

"Concerning the Mechanism of Arbuzov's Rearrangement. XV. Reactions of alpha,beta-Dibromoethylalkyl Esters With Triisopropylphosphites" by V. S. Abramov and A. I. Bol'shakova, Kazan Chemicotechnological Institute imeni S. M. Kirov, Zhurnal Obshchey Khimii, No 2, Feb 57, pp 441-444

Triisopropylphosphite reacts with alpha,beta-dibromoethylalkyl esters and with the methyl ester of alpha,beta-dibromopropionic acid in two separate and individual stages, with the formation of an intermediate addition product in the first stage. Thermal decomposition of the intermediate product results in the formation of the isopropyl ester of alpha-alkoxy-beta-bromoethylphosphonic acids. The isopropyl esters of alpha-alkoxyvinylphosphonic acids were prepared. These esters do not polymerize with peroxides, diazoaminobenzene, or zinc chloride. (U)

Sum. 1360

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ABRAMOV, V.S.

"Concerning Mixed Esters of di-tert-(1,1,1-trichloro)butylphosphorous Acid" by V. S. Abramov and V. K. Khayrullin, Kazan Chemicotechnological Institute imeni S. M. Kirov, Zhurnal Obshchey Khimii, No 2, Feb 57, pp 444-449

Steric factors play either a deciding or very important role during the formation of esters of phosphorous acid from tertiary alcohols. Mixed esters of di-tert-(1,1,1-trichloro)-butylphosphorous acid were prepared from primary and secondary alcohols and phenol. With tertiary alcohols, phosphites did not form. Mixed esters of di-tert-(1,1,1-trichloro)-butylphosphorous acid form complex compounds with cuprous chloride. (U)

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AUTHORS: Abramov, V. S. Kazan Chemicotechnological Inst.

TITLE: Reaction of Dialkylphosphorous Acids with Aldehydes and Ketones. Part 10. Esters of Alpha-oxy-Nitrobenzylphosphinic Acids (O vzaimodeystvii dialkylfosforistykh kislot s al'degidami i ketonami. X. Efiry alpha-oksi-nitrobenzilfosfinovykh kislot)

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 27, No. 1, pp. 169-171 (U.S.S.R.)

ABSTRACT: The condensation reaction of dialkylphosphorous acids with nitrobenzaldehydes was investigated. The addition of the catalyst, in the form of a methyl alcohol-sodium alcoholate solution, brings about a change in the color of the reaction mixture from green to blue. During the blending of dialkylphosphorous acids with nitrobenzaldehydes, no heat liberation was observed. Long term storage of the reaction mixture at room temperature or a somewhat increased temperature led to the formation of esters of alpha-oxynitrobenzylphosphinic acid; the esters gradually crystallize in the liquid reagent mixture. The condensation of the acids with the benzaldehydes can be accelerated provided metallic or diethylphosphorous sodium are used in the role of catalyst; in this case the reaction lasts several days. Since the rates of the condensation reactions described are slow in comparison with other

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Reaction of Dialkylphosphorous Acids with Aldehydes and Ketones

type reactions, it was impossible to draw any conclusions regarding the effect of the nitro-group on the reaction process. The derivation of nine different esters of alpha-oxynitrobenzylphosphinic acids is reported. The condensation reactions of dialkylphosphorous acids with aldehydes and ketones with sodium alcoholate as catalyst in an alcohol solution are unusually rapid and followed by great heat liberation. Condensation reactions without catalysts but with metallic and sodium phosphide take place without heat liberation and are of long duration. Two tables. There are 8 references, of which 6 are Slavic.

ASSOCIATION: The Kazan' Chemical-Technological Institute (Kazanskiy Khimiko-Tekhnologicheskiy Institut)

PRESENTED BY:

SUBMITTED: November 23, 1955

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APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1"

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ABRAMOV, ~~V.S.~~ PALL, Sh.

Reaction of dialkylphosphorous acids with aldehydes and ketones. Part 11. α-oxy-n-methylbenzylphosphinic acid esters. Zhur. ob. khim. 27 no.1:172 Ja '57. (MLRA 10:6)

1. Kazanskiy khimiko-tekhnologicheskiy institut.
(Phosphinic acid)

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

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AUTHORS: Abramov, V. S. and Kapustina, A. S.

TITLE: Reaction of Dialkylphosphorous Acids with Aldehydes and Ketones. Part 12. Esters of alpha-oxy-alpha-furfurylphosphinic and alpha-oxy-alpha-thenylphosphinic acids (O vzaimodeystvii dialkilfosforistykh kislot s al'degidami i ketonami. XII. Efiry alpha-oksi-alpha-furfurilfosfinovoy i alpha-oksi-alpha-tenilfosfinovoy kislot)

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 27, No. 1, pp. 173-176 (U.S.S.R.)

ABSTRACT: This report describes the results obtained during the reaction of dialkylphosphorous acids with furfurole and alpha-thiophene aldehyde. It was established that furfurole and alpha-thiophene aldehyde with dialkylphosphorous acids can react either by the carbonyl group or by the double carbon/carbon bond and possibly also by the conjugated system of double bonds. Investigation showed that dialkylphosphorous acids react by the carbon/carbon bond yielding esters of alpha-oxyfurfurylphosphinic and alpha-oxy-alpha-thenylphosphinic acid with sulfur substituting for oxygen in the ring for thiophene aldehyde. The properties of the esters obtained are listed in Table 2. Data pertaining to the catalysts used in the condensation reactions are listed.

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

AUTHORS: Abramov, V. S. and Bol'shakova, A. I. 79-2-35/58

TITLE: The Mechanism of the Arbuzov Regrouping. Part 4. Reaction of alpha, beta-Dibromoethylalkyl Esters with Triisopropylphosphite (K voprosu o mekhanizme Arbuzovskoy peregruppirovki. IV. Vzaimodeystviye alfa-beta-dibrometilalkilovykh efirov s triizopropilfosfitom).

PERIODICAL: Zhurnal Obshchey Khimii, 1957, vol 27, No 2, pp. 441-444 (U.S.S.R.).

ABSTRACT: It was established experimentally that triisopropylphosphite exposed to alpha,beta-dibromethylmethyl, alpha,beta-dibromodiethyl, alpha,beta-dibromo ethylbutyl ethers and methyl ether of alpha-beta-dibromopropionic acid reacts in two separate stages forming an intermediate addition product in the first stage. The reaction was studied by the changes in the physical characteristics: coefficient of light refraction, specific weight and surface tension which varied with time and in relation to the composition of the reaction mixture. The surface tension was determined by the method of maximum bubble pressure. Thermal decomposition of the addition products gave isopropyl ethers of alpha-alkoxy-beta-bromoethyl phosphinic acids.

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The Mechanism of the Arbuzov Regrouping. Part 4. 79-2-35/58

The polymerizability of the ethers obtained was investigated and it was found that their molecule has possibly a polar character. The ethers investigated did not submit to polymerization with peroxides, diazoaminobenzene and zinc chloride. The negative results are explained either by the steric hindrances or by the weakening of the double bond polarity or by the alkoxy group.

4 tables. There are 4 references, of which 3 are Slavic.

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SUBMITTED: February 2, 1956

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

AUTHORS: Abramov, V. S. and Khayrullin, V. K. 79-2-36/58

TITLE: About Mixed Esters of Di-Tert.-(1,1,1-Trichloro)-Butylphosphorous Acid (O smeshannykh efirakh di-tret.-(1,1,1-trikhlor)-butilfosforistoy kisloty)

PERIODICAL: Zhurnal Obshchey Khimii, 1957, vol 27, No 2, pp. 444-449 (U.S.S.R.)

ABSTRACT: Report describes the syntheses of mixed esters which were obtained from monoacid chlorides of di-tert.-(1,1,1-trichlorobutylphosphorous acid and various alcohols in the presence of pyridine in a dry ether medium. It was established that the steric factors play an essential and possibly even a decisive role in the formation of phosphorous acid esters from tertiary alcohols. The reaction, carried out at a temperature of 0 - 5° with consequent heating of the ester to a boiling point, utilized primary alcohols of normal and iso-structure as well as secondary, cyclic and tertiary alcohols. It was found that primary alcohols of normal structure - methyl, ethyl, propyl, butyl and octyl do react in cold state with the acid chloride resulting in the formation of homologous mixed ester and separation of pyridine chloride. Reactions with tertiary

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79-2-36/58

About Mixed Esters of Di-Tert.-(1,1,1-Trichloro)-Butylphosphorous Acid

alcohols formed no phosphites. The physico-chemical properties of the esters are listed.

It is shown that primary alcohols - isobutyl and fury and secondary alcohols - isopropyl, sec.-butyl and cyclohexanol react with mono acid chloride of di-tert.-(1,1,1-trichloro)-butylphosphorous acid in the presence of pyridine yielding homologous mixed esters (high yields). Mixed esters of butyl-phosphorous acid with copper monochloride form complex compounds.

2 tables. There are 13 references, of which 8 are Slavic

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SUBMITTED: February 2, 1956

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Distr: 4E4J/4E3J/4E2J(J)

√ Mixed system of [illegible]

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

ABRAMOV, V.S.; KHAYRULLIN, V.K.

Reaction of dialkylphosphorus acids with aldehydes and ketones. Part 14: Tertiary-(1,1,1 - trichloro)-butyl-1-trichloromethylcyclohexyl-1 esters of substituted α -oxymethylphosphinic acid. Zhur. ob. khim. 27 no.9:2387-2389 S '57. (MIRA 11:3)

1.Kazanskiy khimiko-tekhnologicheskiy institut.
(Esters) (Acids, Organic)

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

AUTHORS: Abramov, V. S. and Pall, Sh.

TITLE: Reaction of Dialkylphosphorous Acids with Aldehydes and Ketones. Part 11. Esters of alpha-oxy-p-methylbenzylphosphinic acid (O vzaimodeystvii dialkilfosforistykh kislot s al'degidami i detonami. XI. Efiry alpha-oksi-p-metilbenzilfosfinovoy kisloty)

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 28, No. 1, p.172 (U.S.S.R.)

ABSTRACT: Experiments are briefly described in which six esters of alpha-oxy-p-methylbenzylphosphinic acid were obtained from the condensation of p-toluene aldehyde with dialkylphosphorous acids. The condensation was carried out by adding drops of sodium methylate solution in methyl alcohol to an equimolecular mixture of p-toluyl aldehyde and dialkylphosphorous acid. The condensation reaction was rapid with greater heat separation and the reaction rate was approximately the same as that of dialkylphosphorous acids with benzaldehyde. The properties of the asters obtained are described in table. The esters are easily soluble in alcohol but practically insoluble in cyclohexane.
One table. There are two Slavic references.

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P.P. Ramov, U.S.

Academician A. E. Arbuzov. V. S. Abramov (S. M. Kirov Chem.-Technol. Inst., Kazan). *Priroda* 46, No. 9, 31-9(1957).—A biography and brief review of his work on the occasion of his 80th birthday. M. C.

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

AUTHOR: Abramov, V. S. 20-117-5-23/54

TITLE: The Condensation of the Dialkylphosphorous Acids with Carboxylic Acid Derivatives (O kondensatsii dialkilfosforistykh kislot s proizvodnymi karbonovykh kislot)

PERIODICAL: Doklady AN SSSR, 1957, Vol. 117, Nr 5, pp. 811-812 (USSR)

ABSTRACT: After the study of the acids with carbonyl compounds mentioned first in the title the author draws the conclusion that aldehydes and then ketones react most easily. As it was said in former papers of the author (reference 1, 2) some compounds which have an aldehyds group connected with an alkoxy group do not react with aldehydes and ketones. Further works, however, were successful: especially thiourea enters into reactionswith the acids in question. Since thiourea is a base, it can form salts with the dialkylphosphorous acids. Another possible course of reaction is the addition of these acids to the >C= S-binding, analogous to the addition of the acids in question to the carbonyl group. In this case the di-amino-sulphhydryl-methyl-phosphinic acid-ethers are formed. The experiments showed that thiourea reacts with the dialkylphosphorous acids in the case of heating up to a

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certain temperature. Then a vehement reaction begins with self heating of the reaction mass, e. g. with the dimethylphosphorous acid. The reaction of the dialkylphosphorous acids with thiourea occurs without catalyst and the more easily and energetically the smaller the radical of the dialkylphosphorous acid is. The salts of the dialkylphosphorous acids belong to the derivates of the trivalent phosphorus. The addition reactions e. g. of sulphur, are characteristic of them. This is not the case here. Thus the addition to the $>C=S$-binding is more probable. This assumption necessitates further proofs. The constants of the produced substances are given in table 1. These ethers are well soluble in water, alcohol, and other solvents, and can be crystallized only with difficulties. The crystals are similar to paraffin and greasy. Their melting temperature is somewhat extended. The yields of the raw products are good, however, there are great losses in the recrystallization. Tiourea reacts also with other phosphorous acids. With dialkylphosphorous acids react also: urea, formamide, and other derivates of the carboxylic acids. There are 1 table

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The Condensation of the Cialkylphosphorous Acids with Carboxylic Acid Derivatives 20-117-5 23/54

and 4 references, all of which are Slavic.

ASSOCIATION: Chemical-Technological Institute imeni S. M. Kirov, Kazan' (Kazanskiy khimiko-tekhnologicheskiy institut imeni S. M. Kirova)

PRESENTED: June 19, 1957, by B.A. Arbuzov, Academician

SUBMITTED: June 12, 1957

Card 3/3

APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1"

"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

AUTHORS: Abramov, V. S., Belokon, L. Sh., Makhmutova, F. I. 79-28 3-22/61

TITLE: The Reaction of Dialkylphosphorous Acids With Aldehydes and Ketones (O vzaimodeystvii dialkilfosforistykh kislot s al'degidami i ketonami)
Esters of 1-Oxy-1-Acetoethylphosphinic- and 2-Oxy-4-Keto - 2 - Amylphosphinic Acid (Efiry 1-oksi--1-atsetoetilfosfinovoy i 2-oksi-4-keto-2-amilfosfinovoy kislot)

PERIODICAL: Zhurnal Obshchey Khimii, Vol. 28, Nr 3, pp. 665-667 (USSR), 1958

ABSTRACT: The authors carried out systematic investigations of the condensation of dialkylphosphorous acids with diacetyl- and acetylacetone. In this the formation of two products with one or two carbonyl groups was to be expected. In α-diketones (diacetyl) these groups interact by increasing polarization which would have to lead to a condensation of the above mentioned acids with the first carbonyl group of diacetyl under the formation of the compound (I). The reaction of the

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The Reaction of Dialkylphosphorous Acids With Aldehydes and Ketones. 79-28 3-22/61
Esters of 1-Oxy-1-acetoethylphosphinic- and 2-Oxy-4-keto - 2 - Amyl-phosphinic Acid

second carbonyl group with the second molecule of the acid must be independent of the action of the phosphone group on the reactivity of the molecule and on the possibilities of spatial arrangement formed from it after its entrance into the molecule (II). The equimolecular condensation of dialkylphosphorous acids with diacetyl proceeds well, also without catalyst, on the water bath within from 10-12 hours. The vacuum distillation of the esters takes place without decomposition. Contrary to the condensation products of dialkylphosphorous acids with monoaldehydes and monoketones the synthetized esters have a constant boiling temperature. The esters of the 1-Oxy-1-acetoethylphosphinic acid are given in table 1. The condensation of dialkylphosphorous acids with acetyl-acetone must take place under formation of the esters of the 2'-amylphosphine derivatives. In the condensation of dialkylphosphorous acid with a carbonylgroup of acetyl-acetone an ester is formed in its carbonyl form, namely one of

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The Reaction of Dialkylphosphorous Acids With Aldehydes and Ketones. 79-28 3-22/61
Esters of 1-Oxy-1-Acetoethylphosphinic- and 2-Oxy-4-keto - 2 - Amyl-phosphinic Acid

the 2-Oxy-4-keto -2-amylphosphinic acid (III). With the enole form of acetylacetone, however, a 2,4-dioxy-2-penten-3-yl-phosphinate is formed (IV). In both cases the reaction leads to one and the same product with two tautomeric formulae being in equilibrium. The equimolecular condensation of dialkylphosphorous acids with acetylacetone proceeds a little more difficultly without a catalyst than with diacetyl, the yields being small (table 2). The authors tried in vain to determine the carbonylgroup by means of phenylhydrazone. There are 2 tables and 2 references, which are Soviet

ASSOCIATION: Kazanskiy khimiko- tekhnologicheskiy institut (Kazan' Chemical Technological Institute)

SUBMITTED: March 5, 1957

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79-28-4-59/60

AUTHORS: Abramov, V. S., Vil'chinskaya, A. R., Frinovskaya, V. A.

TITLE: In Memoriam Andrey Ivanovich Lun'yak (Pamyati Andreya Ivanovicha Lun'yaka)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol.28, Nr 4, pp.1118-1119 (USSR)

ABSTRACT: On October, 15th, died after long serious disease the 76-year-old Professor for Chemistry at the Medical Institute Kazan', Andrey Ivanovich Lun'yak. He was a pupil of A. M. Zaytsev. Andrey Ivanovich Lun'yak was born on December 17th, 1881, in Petersburg. After finishing high school in Odessa he entered the Military Medical Institute in Petersburg. Then he came as army surgeon to Kazan'. Already 2 years later he left the army and devoted his life to chemistry. He came as laboratory assistant to the Laboratory for Organic Chemistry at the Kazan' University which stood under the leadership of A. M. Zayetsev. Here he passed - thanks to mediation of the university - his pharmacist examination with special permission. In 1908 A. I. Lun'yak was sent to Berlin for 2 years where he worked in the laboratory of E. Fischer. Then he was appointed private docent of the Kazan' University, short time

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79-28-4-59/60

In Memoriam Andrey Ivanovich Lun'yak

afterwards assistant professor for organic chemistry and agricultural analysis in Alexandriya, where he finished his dissertation. From 1916 till 1924 A. I. Lun'yak was professor for physiological chemistry at the new-opened university of Perm'. He was simultaneously dean of the faculty for physics and mathematics and of the medical faculty and later representative of the rector of the university. In 1924 he was appointed professor for the chair for technical chemistry of the Kazan' University, two years later rector of the university. From 1930 on Lun'yak was professor for organic chemistry of the technological faculty of the Chemical-Technological Institute of Kazan'. 6 years later he was appointed leader of the chair for organic chemistry at the Medical Institute of Kazan, where he held lectures for many years. In 1952 A. I. Lun'yak had to retire because of his bad health, was, however, always very interested in the life at the Institute. Andrey Ivanovich Lun'yak was a very good organizer and his energy was inexhaustible. He also took part actively in the development of the chemical industry of the Tatar Republic. Party and government estimated highly his services and he was awarded the Lenin Order. His pupils and assistants will always remember him.

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

SOV/79-28-11-34/55

AUTHORS: Abramov, V. S., Semenova, N. A.

TITLE: On the Interaction Between Dialkyl Phosphorous Acids With Aldehydes and Ketones (O vzaimodeystvii dialkilfosforistykh kislot s al'degidami i ketonami) XVIII. Phenyl-α-Oxyalkyl Phosphinates (XVIII. Fenilovyye efiry α-oksialkilfosfinovykh kislot)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 11, pp 3056 - 3058 (USSR)

ABSTRACT: The synthesis of diphenyl phosphorous acid, which according to earlier experiments (Ref 1) is difficult, was avoided by the easy synthesis of the phenyl ester of phosphorous acid, and made it possible to use the Arbuzov saponification reaction for the synthesis of this acid. Furthermore also the synthesis of the phenyl-α-oxyalkyl phosphinates could be realized by way of this saponification in the presence of compounds with a carbonyl group (Ref 1). The formation of the diphenyl phosphorous acid then takes place according to scheme 1. This acid formed in tautomeric form is condensed with aldehydes and ketones, in the presence of which

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On the Interaction Between Dialkyl Phosphorous Acids With Aldehydes and Ketones. XVIII. Phenyl-α-Oxyalkyl Phosphinates SOV/79-28-11-34/55

a saponification takes place according to scheme 3. The subsequent saponification reactions and condensations are mostly of exothermal character. The forming phenyl-α-oxyalkyl phosphinates are mostly separated in crystalline form after the removal of the phenol formed in the saponification. The saponification reactions of the ethyl ester of phosphorous acid in the presence of benzaldehyde and cyclohexanone under the same conditions do not yield any esters of the α-oxyalkyl phosphinic acids. The synthesized phenyl esters of various α-oxyalkyl phosphinic acids are given in the table. There are 1 table and 7 Soviet references.

ASSOCIATION: Kazanskiy Khimiko-tekhnologicheskiy institut imeni S.M. Kirova (Kazan' Chemical Technological Institute imeni S.M.Kirov)

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

AUTHORS: Abramov, V. S., Kashirskiy, M. I. SOV/79-28-11-35/55

TITLE: On the Reaction of Aryl (Alkyl) Phosphinic Acids With Aldehydes and Ketones (O vzaimodeystvii aril(alkil) fosfinistykh kislot s al'degidami i ketonami) XIX. Esters of the α-Oxyalkylphenyl Phosphinic Acids (XIX. Efiry α-oksialkilfenilfosfinovykh kislot)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 11, pp 3059-3061 (USSR)

ABSTRACT: Abramov showed in an earlier paper (Ref 1) that the dialkyl phosphorous acids are easily affiliated to the $>C=O$ bond of the carbonyl group of the aldehydes and ketones, and form α-oxyaklyl phosphinates. It was only natural also to use these results in the acid esters of aryl and alkyl phosphinic acids, hoping that they, too, would easily enter the reactions with the carbonyl compounds like the dialkyl phosphorous acids. The condensation of these acid esters with aldehydes and ketones must lead to the α-oxyalkylaryl (alkyl)phosphinates according to the following scheme:

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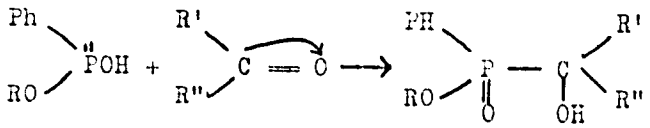
On the Reaction of Aryl(Alkyl)Phosphinic Acids With Aldehydes and Ketones. XIX. Esters of the α-Oxyalkylpheryl Phosphinic Acids SOV/79-28-11-35/55



In the reaction of the acid esters of the phenyl phosphinic acid with aldehydes and ketones the α-oxyalkylphenyl phosphinates formed. The reactions with aldehydes take place under warming, that with ketones under a decrease in temperature. This decrease in temperature has been several times observed in the dissolution of various compounds in dialkyl phosphorous acids. Alkali compounds as catalysts are of only weak effect on the reaction process. The reactions were therefore carried out only when heated on the water bath. The occurrence and the growth of the crystals of the forming ester was the proof of the proceeding reaction. The α-oxyalkylphenyl phosphinates were purified by recrystallization. Their constants

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On the Reaction of Aryl(Alkyl)Phosphinic Acids With Aldehydes and Ketones. XIX. Esters of the α-Oxyalkylphenyl Phosphinic Acids SOV/79-28-11-35/55

are given in the table. The affiliation of the aldehydes and ketones to the carbonyl group can therefore successfully be used in the dialkyl phosphorous phenyl (alkyl) phosphinic and dialkyl(aryl) phosphinic acids; it is of general character. 11 esters of various α-oxyalkylphenyl phosphinic acids were synthesized. There are 1 table and 2 references, 1 of which is Soviet.

ASSOCIATION: Kazanskiy khimiko-tekhnologicheskiy institut imeni S.M. Kirova (Kazan' Chemo-Technological Institute imeni S.M. Kirov)

SUBMITTED: October 31, 1957

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APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1"

"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

5(3)

SOV/62-59-1-6/38

AUTHORS: Arbuzov, A. Ye., ~~Abramov, V. S.~~

TITLE: The Problem of the Effect of Halogen-Substituted Ethers on the Salts of Dialkyl Phosphites (K voprosu o deystvii galoidozameshchennykh prostykh efirov na soli dialkilfosforistykh kislot)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 35 - 40 (USSR)

ABSTRACT: The experimental investigations carried out by the authors have shown that the monochloro-methyl ether reacts regularly with sodium diethyl phosphite and forms ethyl ethers of the methoxy-methyl phosphinic acid. Sodium dimethyl phosphite reacts with monochloro- and monobromo-methyl ether in a similar way as sodium diethyl phosphite and yields the methyl ester of the methoxy-methyl phosphinic acid. In the distillation of reaction products of the bromo-methyl ether with sodium dialkyl phosphite a reaction takes place without separation of the sodium bromide formed in the reaction in which salts of acid esters of the methoxy-methyl phosphinic acid are formed. Monobromo-methyl ether reacts with silver

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

The Problem of the Effect of Halogen-Substituted Ethers on the Salts of Dialkyl Phosphites SOV/62-59-1-6/38

dialkyl phosphites in the same way as with sodium salts and forms corresponding esters of the methoxy-methyl phosphinic acid. The reaction in benzene takes place with a preliminary dissolution of silver salt and apparently forms an adduct of the halogen-substituted ether at silver dialkyl phosphite. In the reaction of chloro-methyl ether with silver dialkyl phosphites the silver salt is equally dissolved and an adduct is presumably formed. On heating the product obtained separates silver chloride and apparently mixed esters of the phosphite. They are disproportionated in the distillation and yield phosphites which contain the same radicals as the silver salts. By the influence of triphenyl methane upon adducts of the chloro-methyl ethers at silver diethyl phosphite the triphenyl-methyl phosphinic acid is formed after saponification. The same reaction with the adduct of the bromo-methyl ether at silver diethyl phosphite, however, yields triphenyl carbinol. This indicates a different course of both reactions. There are 12 references, 10 of which are Soviet.

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26199
S/081/61/000/012/028/028
B103/B202

15.8110

AUTHORS: Abramov, V. S., Tsivunin, V. S.

TITLE: Esters of vinyl phosphinic acid and their polymerizability

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 12, 1961, 715, abstract 12P140. (Tr. Kazansk. khim.-tekhnol. in-ta, 1959, vyp. 26, 96-103)

TEXT: The authors synthesized isobutyl ester of β-bromo ethyl phosphinic and vinyl phosphinic acid. In the polymerization of the diisobutyl ester of vinyl phosphinic acid (I) a viscous colorless compound with low degree of polymerization is formed in the mass (initiator - benzoyl diazoperoxide or paraphon, temperature 80-90°C). In the block copolymerization of I with styrene or methyl methacrylate (temperature 6 and 90°C, respectively, initiator - benzoyl peroxide) solid or rubber-like products are formed with low combustibility and self-extinguishability. The following formulas of the copolymers (I) and (II) are suggested:

$$\{[-CH(C_6H_5)CH_2-]_{63}CH_2CH(R)-\} \quad I,$$

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Esters of vinyl phosphinic acid ...

$$\{[-CH_2C(CH_3)(COOCH_3)-]_{28}CH_2CH(R)-\} \quad II,$$

$$\{[-CH(C_6H_5)CH_2-]_{25}CH(R)CH_2-\} \quad III.$$

A thermoplastic copolymer (in the form of latex) corresponding to formula (III) where R $(iso\text{-}C_4H_9O)_2P{=}O$ was obtained in the emulsion polymerization of (I) with styrene (20-100°C, 20 hr, initiator: paraphon). [Abstracter's note: Complete translation.]

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APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1"

"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

ABRAMOV, V.S.; MAYKOVA, A.I.

Synthesis of mixed alkylalkoxyethylphosphorous acids and study of their properties. Trudy KKHTI no.26:104-108 '59. (MIRA 15:5)
(Phosphorous acid)

APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1"

"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

31550
S/081/61/000/022/022/076
B110/B138

53630 2220, 2209

AUTHORS: Abramov, V. S., Maykova, A. I.

TITLE: Synthesis of mixed dialkyl-α-alkoxy-β-dichloro vinyl esters of phosphoric acid

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 22, 1961, 206, abstract 22Zh230 (Tr. Kazansk. khim.-tekhnol. in-ta, no. 26, 1959, 109-116)

TEXT: $(RO)_2P(O)OC(OR')=CCl_2$ (II) was obtained from the reaction of $(RO_3)P$ with CCl_3COOR' (I). The following is indicated: R, R', yield in %, boiling point in °C/mm, n_D^{20}, d_4^{20}: C_2H_5, CH_3, 27.5, 139-142/7, 1.4520, 1.3020. C_3H_7, CH_3, 50, 135-138/3, 1.4526, 1.2294. iso-C_3H_7, CH_3, 52, 142-143/11, 1.4478, 1.2179. C_4H_9, CH_3, 68.7, 145-146/3, 1.4530, 1.1830. iso-C_4H_9, CH_3, 62.7, 130-132/1.5, 1.4518, 1.1830. C_2H_5, C_2H_5, 40. 103,0.5, 1.4284,-. iso-C_3H_7, C_2H_5, 45, 116.5-118/2, 1.4468, 1.1904. C_4H_9, C_2H_5, 49,

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

31550

Synthesis of mixed dialkyl-α-alkoxy... S/081/61/000/022/022/076
B110/B138

145-147/2, 1.4523, 1.1617. iso-C_4H_9, C_2H_5, 43, 135-136, 5/1, 5, 1.4499, 1.1596. C_2H_5, iso-C_3H_7, 26, 130-131/2, 1.4511, 1.2252. iso-C_3H_7, 41.8, 120-121/2, 1.4445, 1.1720. C_4H_9, C_4H_9, 48, 158-159/2, 1.4530, 1.1317. iso-C_4H_9, C_4H_9, 53, 146-147/2, 1.4498, 1.1199. iso-C_4H_9, iso-C_4H_9 (IIa), 33, 144-146/2, 1.4500, 1.1237. 0.1 mole of I is added dropwise to 0.1 mole of $(RO)_3P$ while heating and stirring, and II is separated after 1-2 hr of heating. In addition, high-boiling products are formed. 1.4 g of Na is added to 15 ml of absolute iso-C_4H_9OH, and 10 g of IIa is added during cooling. The mixture is distilled after heating and $(\text{iso-}C_4H_9O)_3PO$ is separated with a 42.5 yield. Although the reaction of $(RO)_2P(O)H$ and I was observed, it was not possible to separate any reaction products. [Abstracter's note: Complete translation.]

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

5(3) SOV/79-29-4-39/77

AUTHORS: Abramov, V. S., Khayrullin, V. K.

TITLE: On the Reaction of Dialkylphosphorous Acids With Aldehydes and Ketones (O vzaimodeystvii dialkilfosforistykh kislot s al'degidami i ketonami). XIX. Di-1-trichloromethyl Cyclopentyl-1 Esters of α-Oxyalkyl Phosphinic Acids (XIX. Di-1-trikhlormetiltsiklopentil-1-ovyye efiry α-oksialkilfosfinovykh kislot)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1222-1225 (USSR)

ABSTRACT: The report under review is a continuation of previous papers published by the authors on the condensation of dialkylphosphorous acids with carbonyl compounds, a process which is becoming increasingly important. The reaction of tertiary chlorine-substituted alcohols with PCl_3 results in the acid dichlorides and acid monochlorides of the corresponding alkyl- and dialkylphosphorous acids. Such acid chlorides were obtained by the authors from 1-trichloromethyl cyclopentanol-1 (Ref 5) as well. Acid monochlorides change with water into the corresponding dialkylphosphorous acids. Di-1-trichloromethyl cyclopentyl-1-phosphorous acid was characterized as a viscous non-distillable liquid. It corresponds to the empirical formula $C_{12}H_{17}O_3Cl_6P$.

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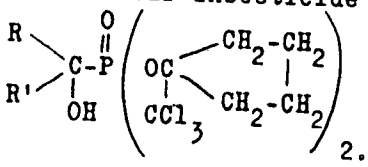
SOV/79-29-4-39/77

On the Reaction of Dialkylphosphorous Acids With Aldehydes and Ketones. XIX. Di-1-trichloromethyl Cyclopentyl-1 Ester of α-Oxyalkyl Phosphinic Acids

When left undisturbed it forms crystals with a melting point of 37-38°. This acid condenses with aldehydes and ketones without catalyst. This reaction takes place, at room temperature, within 21-50 hours, and much faster at temperatures between 40 and 60°. In order to ensure complete crystallization the condensation products (e.g. with propionic-, butyric-, and isovaleric aldehyde) had to be left undisturbed for a while. The authors assume that the reaction takes place with a trivalent form of phosphorous acids. Thus the di-1-trichloromethyl cyclopentyl-1 esters of the substituted α-oxymethylphosphinic acids were obtained by the condensation of the above acid with aldehydes and ketones. The constants and analyses of the esters obtained are given in the table. Some esters will still have to be examined as to their insecticide activity.



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SOV/79-29-4-39/77

On the Reaction of Dialkylphosphorous Acids With Aldehydes and Ketones. XIX. Di-1-trichloromethyl Cyclopentyl-1 Ester of α-Oxyalkyl Phosphinic Acids

There are 1 table and 5 references, 4 of which are Soviet.

ASSOCIATION: Kazanskiy khimiko-tekhnologicheskiy institut (Kazan' Institute of Chemical Technology)

SUBMITTED: March 25, 1958

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

5 (3)

AUTHORS: Abramov, V. S., Khayrullin, V. K. SOV/79-29-5-41/75

TITLE: On the Reaction of Dialkyl-phosphorous Acids with Aldehydes and Ketones (O vzaimodeystvii dialkilfosforistykh kislot s al'degidami i ketonami). XX. Esters of Some α-Oxyalkyl-thiophosphinic Acids (Efiry nekotorykh α-oksialkiltiofosfinovykh kislot)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1599-1604 (USSR)

ABSTRACT: The scheme of the reactions mentioned in the title was largely clarified by the authors and other scientists (Refs 1-5). It was to be expected that the thioderivatives of dialkyl-phosphite react with aldehydes and ketones in a similar way. Only few data on this problem are available in publications (Ref 6). This may be due to the fact that the preparation of dialkyl-thiophosphites was difficult in the beginning. Only quite recently (Ref 8) it was reported that by the influence of hydrogen sulfide upon halides of organically substituted phosphoric acids in the presence of tertiary bases thiopyroderivatives are formed and dialkyl-chloro-phosphites and their analogs in this reaction give

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dialkyl-thiophosphorous acids in good yield. According to this reaction scheme, the authors prepared dialkyl- and diaryl-thiophosphites and condensed them with aldehydes and ketones. The condensation takes 15-200 hours at room temperature. The condensation products mostly represent highly viscous, sirupy liquids or vitreous substances. Some of these liquids could be recrystallized from acetone. As dialkyl-thiophosphites and dialkyl-phosphites are occurring in two tautomeric forms, it is assumed that the reaction with the enol form proceeds by reaction of the single electron pair of trivalent phosphorus with the electrophilic carbon atom of the carbonyl group. Like the esters of α-oxy-alkyl-phosphinic acids also the esters of α-oxy-alkyl-thiophosphinic acids undergo a cleavage of the P-C-bond due to heating and influence of lyes. This is explained by the existence of an intremolecular hydrogen bond (Refs 5, 11). A table presents the reaction times, melting points, and analytical data of the following compounds: Phenyl ester of α-oxy-(-β,β,β-trichloro)-ethyl-thiophosphinic acid; tertiary-(1,1,1-trichloro)-butyl ester of the same acid;

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On the Reaction of Dialkyl-phosphorous Acids With Aldehydes and Ketones. XX. Esters of Some α-Oxyalkyl-thiophosphinic Acids SOV/79-29-5-11/71

tertiary-(1,1,1-trichloro)-butyl ester of α-oxy-benzyl-thiophosphinic acid; the same trichloro-butyl ester of α-oxy-isopropyl-thiophosphinic acid; the same trichloro-butyl ester of α-oxy-cyclopentyl-thiophosphinic acid; 1-trichloro-methyl-cyclopentyl ester of α-oxy-benzyl-thiophosphinic acid; the same ester of α-oxy-m-nitrobenzyl-thiophosphinic acid; the same ester of α-oxy-isopropyl-thiophosphinic acid, and the same ester of α-oxy-cyclohexyl-thiophosphinic acid. The experimental part describes the condensations carried out, the formation of dialkyl-phosphorous acids and the decomposition of the esters by lyes. There are 1 table and 14 references, 12 of which are Soviet and 1 Polish.

ASSOCIATION: Kazanskiy khimiko-tekhnologicheskiy institut (Kazan' Institute of Chemical Technology)

SUBMITTED: May 7, 1958

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APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1"

"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

5(3)

SOV/79-29-7-53/8

AUTHORS: Khayrullin, V. K., Ledeneva, A. I., Abramov, V. S.

TITLE: Synthesis and Isomerization of the Mixed Esters of Di-β,β'-dichloroisopropylphosphorous Acid. V (Polucheniye i izomerizatsiya smeshannykh efirov di-β,β'-dikhlorizopropilfosforistoy kisloty. V)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 7, pp 2355-2359 (USSR)

ABSTRACT: Interaction of alcohols with PCl_3 yields alkyldichlorophosphites, dialkylchlorophosphites, dialkylphosphorous acid, and trialkylphosphites depending on the nature of the radical, the presence of substituents, and reaction conditions. Treatment of chlorine- and cyanine-substituted alcohols (Refs 2, 3 respectively) with PCl_3 gives acid chlorides of phosphorous acid and in some cases phosphites. The α,γ-dichlorhydrin of glycerin was used for this investigation. The compound reacted with PCl_3 at room temperature and gave the following compounds: The acid dichloride of β,β'-dichloroisopropylphosphorous acid (22%), the acid monochloride of di-β,β'-dichloroisopropylphosphorous acid (25.4%), and the di-β,β'-dichloroisopropyl ester of

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β, γ-dichloropropylphosphinic acid (9.8%). According to M. I. Kabachnik and P. A. Rossiyskaya (Ref 4), the latter is formed by an inter- or intra-molecular isomerization of the tri-β, β'-dichloroisopropylphosphite. The reaction of the α, γ-dichlorohydrin of glycerin with PCl_3 is demonstrated in the scheme given. The intact phosphorous ester, which was not obtained in pure form, reacted with cuprous chloride. This may be regarded as proof of the existence of phosphite in the solution (Ref 5). The acid monochloride of di-β, β''-dichloroisopropylphosphorous acid was saponified with water, and the resulting substituted phosphorous acid condensed with aldehydes and ketones. The acid dichloride of the same acid was used for synthesizing the mixed esters of phosphorous acid by treatment with aliphatic alcohols in absolute ether in the presence of pyridine at -6 - 0° (yield 47-65%). The physical properties of the synthesized esters are given in table 1

$$\begin{matrix} CH_2Cl \\ CH_2Cl \end{matrix}\!\!>CHOP(OR)_2 \quad ,$$

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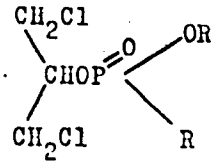
Synthesis and Isomerization of the Mixed Esters of Di-β, β'-dichloroisopropylphosphorous Acid. V SOV/79-29-7-53/[illegible]

those of the alkyl-β, β'-dichloroisopropyl esters of the alkylphosphinic acids in table 2,



There are 2 tables and 8 references, 6 of which are Soviet.

ASSOCIATION: Kazanskiy khimiko-tekhnologicheskiy institut (Kazan' Institute of Chemical Technology)

SUBMITTED: July 3, 1958

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

5(3) SOV/79-29-8-19/81

AUTHORS: Khayrullin, V. K., Ledeneva, A. I., Abramov, V. S.

TITLE: On the Reaction of Dialkyl-phosphorous Acids With Aldehydes and Ketones. XXI. Di-β,β'-dichloro-isopropyl Esters of the Substituted α-Oxymethyl-phosphinic Acid

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 8, pp 2551-2553 (USSR)

ABSTRACT: The authors continued their investigations concerning the synthesis of different α-oxyalkyl-phosphinates by condensation of the dialkyl-phosphorous acids with carbonyl compounds (Ref 1), and extended them to the di-β,β-dichloro-isopropyl-phosphorous acid. They found previously (Ref 2) that condensations which lead to the formation of chlorine-substituted α-oxyalkyl-phosphinates take place also without catalysts at room temperature. The condensation of the β,β'-dichloro-isopropyl-phosphorous acid, and other acids with chlorine atoms in the ester radicals of different structure, is very interesting. The above-mentioned acid was obtained by action of water on the corresponding acid chloride:

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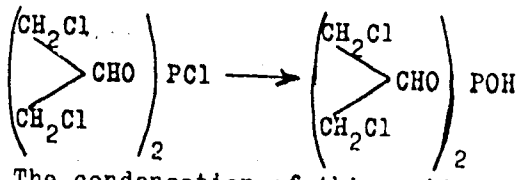
SOV/79-29-8-19/81

On the Reaction of Dialkyl-phosphorous Acids With Aldehydes and Ketones. XXI. Di-β,β'-dichloro-isopropyl Esters of the Substituted α-Oxymethyl-phosphinic Acid



The condensation of this acid with aldehydes and ketones was mostly carried out by mixing equimolar quantities of the reactants, without catalyst, at room temperature. The end products were best separated if they were crystallizable. The formation of a compact crystalline mass indicates the end of the reaction. The data of the esters recrystallized from 96% alcohol are presented in the table (NN° 1-5), in addition to the di-tert.-(1,1,1-trichloro)-butyl esters hitherto unknown of the α-oxy-β-chloro-isopropyl-phosphinic and α-oxy-β,β'-dichloro-isopropyl-phosphorous acids (NN° 6,7). The condensation products of the di-β,β'-dichloro-isopropyl-phosphorous acid with acetic, propionic, butyric, and isovalerianic aldehyde, cyclopentanone, etc., resulted in the form of sirupy liquids the purification of which was difficult. There are 1 table and 2 Soviet references.

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

5(3)

AUTHORS: Abramov, V. S., Il'ina, N. A. SOV/20-125-5-20/61

TITLE: Reactions of Aldehydes and Ketones With Phosphorous Acid Amides (Reaktsii al'degidov i ketonov s amidami fosforistykh kislot)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 5, pp 1027-1029 (USSR)

ABSTRACT: Aldehydes and ketones react with phosphorus trichloride and form products which after the treatment with water or alcohol are transformed into α-oxy-alkyl-phosphinic acids or esters of the latter (Ref 1). This reaction was investigated more thoroughly (Refs 2 - 4). It was proved that aldehydes and ketones react with mono- and di-halogen derivatives of phosphorus with the same positive result. They react as well in the case of heating with phosphonium iodide and yield oxy-alkyl derivatives. Phosphines enter this reaction only in an intense HCl current (Ref 5). Hypophosphorous acid, phosphorous acid, and alkyl-phosphinous acid can react with aldehydes and ketones and yield oxy-substituted phosphorus derivatives (Ref 8). Aldehydes and ketones react with complete esters of phosphorous acid according to the type

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of halogen esters and yield esters of the α-alkoxy-thio--phosphinous acids (Ref 11). It may be assumed that the dialkylamido-(anilido)-phosphites as compounds of trivalent phosphorus are bound to react with the carbonyl compounds in the first place according to the phosphite type (see Scheme). The reaction of the action of aldehydes and ketones upon the last-mentioned phosphites proceeds apparently with the formation of an affiliation intermediate product (II), which has probably the nature of a quasiphosphonium. It is transformed, analogously to the Arbuzov regrouping, into the final product (III) of the reaction. Another course of the reaction is, however, possible as well. The experimental investigation carried out proved that diphenyl-anilido--phosphite, pyrocatechol-anilido-phosphite and other phosphites react very intensely with aldehydes and ketones. A considerable generation of heat occurs already in mixing the components. In some reactions temperature rises to more than 100°. After the cooling the reaction products solidify to a glassy mass which in several cases assumes a yellow

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Reactions of Aldehydes and Ketones With Phosphorous Acid Amides SOV/20-125-5-20/61

color. In the case of constant cooling and mixing the components in portions the reactions proceed moderately and the products remain colorless. Thus reactions of diphenyl- and pyrocatechol-anilido-phosphite with acet-, propion-, and benzaldehyde, acetone, and cyclohexanone were carried out. Products were synthesized which corresponded to the affiliation products according to the empirical formula. Table 1 shows their properties (Nr 1 - 7). Nr 4 and 7 were saponified with diluted HCl at moderate heating. In the first case pyrocatechol and aniline were isolated from the saponification products, in the second case phenol was separated, which was transformed into tibromophenol and aniline. The authors failed in isolating the expected α-oxy-iso-propyl-phosphinic- and 1-phenoxy-cyclohexyl-1--phosphinic acids. They believe that anilido-phosphites react with aldehydes and ketones according to the type of the Arbuzov regrouping. They ascribe to them the structural formulas given in table 1. There are 1 table and 14 references, 6 of which are Soviet.

Card 3/3

Kazan Chem. Tech. Inst.

Submitted: Oct 1958

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

~~5 (3)~~ 5.3630

66423

AUTHORS: Kukhtin, V. A., Abramov, V. S., Orekhova, K. M. SOV/20-128-6-28/63

TITLE: Regrouping of the Esters of X-Oxy-alkyl Phosphinic Acids to Isomeric Phosphates

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 6, pp 1198 - 1200 (USSR)

ABSTRACT: The regrouping mentioned in the title (Refs 1,2) can - according to reference 5 - only take place if X is split off as an anion. Otherwise, a decomposition into aldehyde and dialkyl-phosphorous acids (Ref 6) must occur under the influence of alkalis. A similar regrouping producing isomeric phosphates is mentioned in reference 7 (see Diagram). The 2nd author made dialkyl-phosphorous acids directly act on diacetyl (Ref 8), and obtained esters of the α-oxy-β-aceto-ethyl-phosphinic acid (Table 1, Products A). Under different conditions, products with other constants were obtained. In a glass flask (instead of soldered-up ampullae), dialkyl phosphites with diacetyl yield the products B (Table 1) at a temperature above 100°. Table 2 shows the influence of experimental conditions on the course of reaction with the use of diethyl-phosphorous acid. A comparison of products A and B shows that A contains 8.16% of the hydroxyl group

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Regrouping of the Esters of X-Oxy-alkyl Phosphinic Acids to Isomeric Phosphates SOV/20-128-6-28/63

(according to Tserevitinov's method). Its infrared spectrum shows an intensive band at 3.290 cm^{-1} (Ref 9). Hence it seems to be certain that A is an ester of α-oxy-β-aceto-ethyl-phosphinic acid. The absorption at 3250-3300 cm^{-1} is missing in the infrared spectrum of B. On saponification with barium hydrate, it yields a barium salt of diethyl phosphate and, therefore, is a mixed diethyl-3-keto-2-butyl ester of the phosphoric acid. A diagram shows the interaction reaction of dialkyl-phosphorous acids with diacetyl yielding the isomeric products A or B depending on the conditions of execution. Sodium alcoholate accelerates this reaction and yields product B exclusively. The authors explain the regrouping under review in a way different from reference 5. An accompanying splitting-off of the haloid ion is not necessary. Thus, the authors detected a new interesting regrouping (as mentioned in the title) to isomeric mixed esters of the phosphoric acid. It takes place under the influence of sodium alcoholates in alcoholic solution, or due to the influence of dialkyl phosphites on diacetyl at 125-130°. The names of B. A. Arbuzov, V. S. Abramov and A. S. Kapustina are

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Regrouping of the Esters of X-Oxy-alkyl Phosphinic Acids to Isomeric Phosphates SOV/20-128-6-28/63

also mentioned in the paper. There are 2 tables and 10 references, 5 of which are Soviet.

ASSOCIATION: Kazanskiy khimiko-tekhnologicheskiy institut im. S. M. Kirova (Kazan' Institute of Chemical Technology imeni S. M. Kirov). Kazanskiy filial nauchno-issledovatel'skogo kinofotoinstituta (Kazan' Branch of the Scientific Research Institute of Cinematography and Photography)

PRESENTED: June 12, 1959, by B. A. Arbuzov, Academician

SUBMITTED: June 1, 1959

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

ABRAMOV, V. S., Doc Chem Sci -- (diss) "Investigation of a number of derivatives of α-oxyalkylphosphinic acids." Moscow, 1960. 32 pp; (Academy of Sciences USSR, Inst of Elemento-organic Compounds); 150 copies; price not given; list of authors' work at end of text (34 entries); (KL, 18-60, 146)

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B011/B003

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AUTHORS: Abramov, V. S., Il'ina, N. A.

TITLE: Reaction of Aldehydes and Ketones With the Amides of Phosphorous Acids

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 4, pp. 823-825

TEXT: Until recently the authors assumed that aldehydes and ketones cannot always react with the amido group of the amides of phosphorous acids since merely a small amount of resin could be obtained by such a reaction. In order to verify this assumption the authors examined the reactions of aldehydes and ketones with di-substituted amides of phosphorous acids. They found that aldehydes and ketones react with diethyl amides of phosphorous acids (Ref. 4). The dialkyl amides of phosphorous acids react particularly easily with halogen-substituted carbonyl compounds such as chloral, chloroacetone, symmetric dichloroacetone, et al. As proven by several chemists (Ref. 5), the esters of

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phosphorous acid react with halogen-substituted aldehydes and ketones, thus forming mixed esters of phosphoric acid. The phosphite is primarily attacked by the electrophilic carbon atom of the carbonyl group. Thus, and intermediate with a three-membered ring is formed. It decomposes while the halogen alkyl splits off and mixed dialkylvinyl esters of phosphoric acid are formed (see Scheme). Chloral, chloro acetone, α-chlorocyclohexanone, et al. react easily with diethyl amides of phosphorous acids and form amidoalkylvinylesters of phosphoric acid. They react similarly to the esters of phosphorous acid. The reaction probably starts with an attack of the phosphorus atom containing an undivided electron pair. An intermediate (II) is formed. The reaction is completed by the conversion of the intermediate compound into the amido ester of phosphoric acid and by cleavage of the halogen alkyl. The amidoalkylvinyl esters of phosphoric acid are colorless, mobile, and almost odorless liquids (Table 1). Ten such esters are listed in Table 1. They are able to add bromine. By using the bromide-bromate method the authors found that the double bond in the diethyl amidobutyl isopropenyl ester of phosphoric acid was fully conserved. If

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Reaction of Aldehydes and Ketones With the Amides of Phosphorous Acids

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B011/B003

chlorine is contained in the vinyl radical, the above-mentioned determination does not yield satisfactory results. In their experiments the authors failed to determine the structure of the resulting products by means of exchange of the ester radicals (Ref. 6). Apparently, the diethylamido group bonded to a phosphorus atom has a disturbing effect on the exchange reaction of the mixed alkylamido esters. This reaction is further investigated. The diamido esters of phosphorous acids react with aldehydes and ketones in a similar way as amido esters. There are 1 table and 6 Soviet references.

ASSOCIATION: Kazanskiy khimiko-tekhnologicheskiy institut im. S. M. Kirova (Kazan' Institute of Chemical Technology imeni S. M. Kirov)

PRESENTED: January 23, 1960, by B. A. Arbuzov, Academician

SUBMITTED: January 21, 1960

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

ABRAMOV, V.S.

"Structure and reactivity of dialkylphosphorus acids."

Khimiya i Primenenie Fosfororganicheskikh Soyedineniy (Chemistry and application of organophosphorus compounds). A. [illegible] ed. by Kazan Affil. Acad. [illegible], USSR, Moscow 19[illegible]

Collection of complete papers presented at the [illegible] Chemistry of Organophosphorus Compounds.

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IL'INA, N.A.; LUKOVNIKOVA, A.P.; ABRAMOV, V.S.

Reactions of aldehydes and ketones with phosphorous acid amides. Report No.5: Action of α-chloro-substituted aldehydes and ketones on di-β-chloroethylphosphorous acid diethylamide. Trudy KKHTI no.30:40-44 '62. (MIRA 16:10)

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ABRAMOV, V.S.; SHALMAN, A.L.

Reactions of dialkyl phosphorous acids with aldehydes and ketones. Report No.25: Esters of α-hydroxy-$\beta,\beta,\beta',\beta'$-tetrachloroisopropylphosphinic acid. Trudy KKHTI no.30:45-46 '62. (MIRA 16:10)

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"APPROVED FOR RELEASE: 03/20/2001 CIA-RDP86-00513R000100210015-1

ABRAMOV, V.S.; SHALMAN, A.L.

Interaction of dialkylphosphorous acids with aldehydes and ketones. Part 24: Esters of α-hydroxy-β,β,β'-trichloroisopropylphosphinic acid. Zhur.ob.khim. 32 no.3:827-829 Mr '62. (MIRA 15:3)

1. Kazanskiy khimiko-tekhnologicheskiy institut imeni S.M.Kirova. (Phosphinic acid)

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BARABANOV, V.I.; ABRIMOV, V.S.

Reaction of phosphinic acids with hydrogen cyanide. Part 16: Esters of ethyl(methyl)-α-hydroxy-β,ββ-trichloroethylphosphinic acid, analogs of chloroxuron. Zhur. obshch. 35 no. [illegible] 5-[illegible] p 1965. (MIRA 18:3)

1. Kazanskiy veterinarnyy institut. Submitted [illegible] 1964.

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zene and dioxane, decelerated the reaction but the ester was

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obtained in good yield. The reaction of dialkylphosphorous acids with o- and p-nitrobenzaldehydes leading [illegible]

SUBMITTED: 25Jun64 ENCL: [illegible] SUB CODE: OC, GC

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ABRAMOV, V.S.; IL'INA, N.A.

Rearrangement of amido esters of phosphorous acids in reactions with -halo carbonyl compounds. Action of monochloroacetic acid esters on di-(diethyl)-amidoalkyl esters of phosphorous acid. Dokl. AN SSSR 155 no.1:112-114 Mr '64. (MIRA 17:4)

1. Kazanskiy khimiko-tekhnologicheskiy institut im. S.M.Kirova. Predstavleno akademikom B.A.Arbuzovym.

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ACC NR: AP7000723 SOURCE CODE: UR/0079/66/036/005/0923/0930

ABRAMOV, V. S., DOLGHINA, Z. S., Kazan' Chemicotechnological Institute im. S. M. Kirov (Kazanskiy khimiko-tekhnologicheskiy institut)

23
B

"Synthesis and Properties of Amides of Cyclic Phosphorous Acids"

Moscow, Zhurnal Obshchey Khimii, Vol 36, No 5, 1966, pp 923-930

Abstract: A series of dialkylamides of glycolphosphorous acid and its homologs were synthesized for a systematic study of their properties. The dialkylamides of ethyleneglycolphosphorous acid and propyleneglycolphosphorous acid were found to add sulfur and selenium, forming dialkylamides of glycolthiophosphoric and glycolselenophosphoric acids. Dialkylamides of ethyleneglycolphosphorous acid and its homologs react with cuprous chloride to form complexes. They are readily oxidized by isopropylbenzene hydroperoxide. The infrared spectra of the compounds obtained are discussed. Orig. art. has: 1 figure and 5 tables. [JPRS: 37,023]

TOPIC TAGS: organic amide, phosphorous acid, organic synthetic process, organoselenium compound

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